ISSN 2321-807X

Electrospun Nanofibers of Acrylonitrile and Itaconic Acid Copolymers and their Stabilization

Selda Sen , A. Sezai Sarac*
Istanbul Technical University, Department of Chemistry,
Polymer Science and Technology,Maslak, 34469, Istanbul, Turkey
sarac@itu.edu.tr
*Corresponding author: Prof. Dr. A. Sezai Sarac

ABSTRACT

(APS) as an oxidant in the aqueous medium,and nanofibers produced by electrospinning . Electrospun nanofiber mats were by treated heat under air atmosphere to be stabilized. Nanofiber production from AN-IA copolymers and suitability of the nanofiber as carbon nanofiber precursor is discussed.

Copolymer are characterized using Fourier Transform Infrared - Attenuated Total Reflectance spectrometer (FTIR-ATR), Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR), differential scanning calorimeter (DSC), thermal gravimetric analysis (TGA) and dynamic mechanical analysis (DMA). The effect of IA content on the spectroscopic and thermal properties of AN-IA copolymers was investigated. Increasing IA content confirmed by spectroscopic methods seriously affects thermal properties which is important for carbon nanofiber production. IA provides a catalytic effect on stabilization process by decreasing initiation cyclization reaction temperature from 202 to 195 ^oC.

Elecrospinning from the AN-IA copolymer solutions in dimethyl foramide (DMF) was performed, morphology of nanofibers was monitored using Scanning Electron Microscopy (SEM). Bead free nanofibers were produced from AN-IA copolymer solutions under same conditions. Average nanofiber diameter decreases from 878±18 to 376±7 nm according to increasing IA content in copolymers.

The nanofiber mats produced were treated at high temperature under air atmosphere for oxidative stabilization. Stabilized nanofibers were characterized using FTIR-ATR spectrometer and a new structure was monitored as a result of cyclization reactions. The stabilized nanofibers were also characterized mophologically using SEM. Volume loss occurring after heat treatment calculated based on the nanofiber diameter changes.

Consequently, electrospun nanofibers can be suggested as a carbon nanofiber precursor due to suitability for electrospinning and stabilization process.

Indexing terms/Keywords

Nanofiber; Acrylonitrile; Itaconic Acid; Copolymer

Academic Discipline And Sub-Disciplines

Nanoscience, Polymer,Nanofiber

SUBJECT CLASSIFICATION

Materials,Chemistry

TYPE (METHOD/APPROACH)

Experimental

INTRODUCTION

Polyacrylonitrile (PAN) is an important material for production of both synthetic fibers and high performance fibers, but it is usually modified by copolymerization with small proportions of comonomers such as vinyl acetate, methyl acrylate, methyl methacrylate, acrylic acid and itaconic acid [1-4].

Polyarylonitrile (PAN) fibers are the most widely used precursor for high-property carbon fibers, the important reinforced materials for advanced composites in many fields, such as aerospace, sports, transportation, and petrochemical industry. PAN as a carbon fiber precursor shows some superiorities such as high carbon yield and flexibility for tailoring of the structure of the final product [5].

Thermal behavior of acrylonitrile homo- and copolymers has always been a subject of great interest to improve precursor for the production of carbon fibers. Thermal stabilization, during which ladder structure is formed to enable PAN fibers infusible and nonflammable, is an indispensable process in the manufacture of carbon fibers. For industrial production, thermal stabilization of PAN fibers is usually performed in a temperature range of 200–300^{o}C under certain stretching force in air. Besides temperature and stretching ratio, the comonomers used in PAN precursor are the other main important factor for the quality of carbon fiber [6].

The rapidly developing electrospinning technique provides a straightforward and cost-effective approach to produce micro and/or nanofiber webs of copolymers by applying high voltage to a polymeric solution to create an electrically charged jet. The extrusion force is generated by the interaction between the charged polymer fluid and an external applied electric field. During the electric field application, the electrostatic force overcomes the surface tension and a charged jet is ejected from the tip of the Taylor cone. The polymeric jet is then subjected to instability phenomena that stretch and reduce fiber diameter, before being randomly deposited onto a grounded target [7]. PAN has been used as polymer in electrospinning studies. Based on the morphological studies, average nanofiber diameter has been varied from 200 nm to 1200 nm according to concentration and applied voltage [8-10].

Carbon nanofibers are used for composite applications; beside they have been originally used in other applications as filters, high temperature catalysts, heat management materials in aircraft and semiconductor device. Fabrication process of carbon nanofibers contains nanofiber production of polyacrylonitrile (PAN) precursors, stabilization of nanofibers at 200-400°C in the air and follows carbonization process in inert atmosphere at high temperature (>1000°C) [11]. To produce carbon nanofibers , the electrospinnig method has been used by various researchers effectivelly [11-13]. In these studies, commercial PAN was prefered as precursor mostly. After carbonization process, electrospun PAN based nanofibers exhibited good electrical and mechanical properties related to uniform and continuous fiber formation. The electrical conductivities of the carbonized web could have been improved modifying electrospinning process and carbonization process. Aligned nanofibers carbonized at 1000 and 2200 ^{o}C shows electrical conductivities 180 and 800 S/cm which were measured paralel to bundle axis [11].

The electrospun PAN nanofibers possess high degrees of macromolecular orientations and substantially reduced concentration of structural defects, and the ultra-small diameters may also mitigate the formation of structural inhomogeneities, particularly sheath core structures, during the thermal treatments [14-16]. Electrospun carbon nanofibers are produced through a top-down nano-manufacturing process; they are low-cost, continuous, and also easy to align, assemble, and process into applications.

Itaconic acid as comonomer used in PAN production has been an important material for both commercial applications and scientific research. There are several studies about reaction kinetics, rheology and thermal properties of acrylonitrile-itaconic acid (AN-IA) copolymer. In this study, PAN has been modified with different proportions of IA comonomer. Synthesized AN-IA copolymers were used to produce nanofibers by electrospinning technique first time, to understand the effect of IA on nanofiber or carbon nanofiber production and their acceptability as carbon nanofiber precursor .Acrylonitrile-based copolymers produced free radical polymerization are widely used in the production of acrylic fibers. Polyacrylonitrile fibers suffer from poor hygroscopicity and low dye uptake because of a high degree of ordering, a lack of segmental mobility as a result of a compact structure, and a high glass-transition temperature (T_g). Therefore suitable [20]. comonomers used in the manufacturing of acrylic fibers can be either neutral or ionic,i.e.,s containing sulfonic, phosphoric, or carboxylic acid groups influences both the rate of diffusion and the uptake of cationic dyes. Acidic comonomers not only improve the hygroscopicity but also help in the cyclization of the nitrile group to form a ladder structure during oxidation of acrylic fibers for carbon fiber production [23].

Block copolymers of PAN with polymethacrylonitrile as one component are of potential interest in the development of high-tech devices such as lithography due to their polarity, solubility and high plasma etching resistance properties. Block copolymers can be prepared by means of special techniques like anionic living polymerization [24].

Polymerization of acrylonitrile with different comonomers have been carried out bulk, solution and emulsion polymerization techniques successfully [25-27]. Water-phase precipitation polymerization has been a preferable technique for AN based polymer synthesize to achieve high molecular weight, which is important for mechanical properties of polymer [28,29].

The conversion of PAN precursor fibers to carbon fibers involves an intermediate step of stabilization reaction at 180–400°C. During stabilization, the polymer undergoes physical and chemical changes as a result of of nitrile groups to form an aromatized structure known as a ladder polymer. The acid monomers play a catalytic role in the cyclization process which stabilizes the polymer backbone before carbonization [31].

The copolymerization of AN/IA in the aqueous deposited polymerization system initiated by the single water-soluble initiator-APS was performed [35]. Polymerization temperature and polymerization conversion are the important parameters to affect the monomer reactivity ratios of AN and IA in the aqueous deposited copolymerization system. The monomer reactivity ratios of AN/IA at 60 °C are 0.64 (r_{AN}) and 1.37 (r_{IA}) calculated from Kelen–Tüdõs method, 0.61 (r_{AN}) and 1.47 (r_{IA}) calculated from Fineman–Ross method. At lower polymerization conversion (<5%), the reactivity ratios of AN and IA remains stable. If the polymerization conversion is more than 5%, the monomer reactivity ratio of AN increases, IA decreases.

The copolymerization of AN/IA by the solution polymerization method with dimethylformamide (DMF) was investigated [36]. Copolymerization of AN with IA in DMF and DMF/water mixture was investigated at enhanced concentrations of the latter [27]. The copolymerization of IA/AN is associated with a marked penultimate unit effect for radicals terminated in AN as a result of the copolymer composition analysis. IA radicals have very little reactivity towards its own monomer unit. AN radical has a greater preference to the IA unit than its own monomer. IA retarded the polymerization rate significantly.

Porous AN/IA copolymers were synthesized by suspended emulsion polymerization with potassium peroxydisulfate (KPS) as an initiator, poly(vinyl alcohol) (PVA) as a dispersant agent, and Span80 as an emulsifier [26].

Among various polymers, acrylonitrile-based homo- and co-polymers were most recently fabricated into nanofibrous materials with reinforcing, superhydrophobic and catalytic properties [38]. Electrospinning uses electrostatic forces to produce fine fibers from polymer solutions or melts and the fibers thus produced have a thinner diameter and a larger surface area than those obtained from conventional spinning processes. Furthermore, a DC voltage in the range of several tens of kVs is necessary to generate the electrospinning [38].

In electrospinning process, the solution must gain sufficient charges such that the repulsive forces within the solution are able to overcome the surface tension of the solution. Subsequent stretching or drawing of the electrospinning jet also depends on the ability of the solution to carry charges, in other words the conductivity of solution. Generally, the electric conductivity of solvents is very low (typically between 10^{-3} to 10^{-9} ohm^{-1} m^{-1}) as they contain very few free ions, if any, which are responsible for the electric conductivity of solution. The presence of acids, bases, salts and dissolved carbon dioxide may increase the conductivity of the solvent. The electrical conductivity of the solvent can be increased significantly through mixing chemically non-interacting components. Cetiner and et al. have used electrospinng technique to produce conductive composites from polypyrole that had been polymerized in AN-VAc copolymer matris. The nanofiber diameters and surface morphology show changes according to conductivty of polymeric material [43].

One of the several reasons for electrical discharge of the stored charge through the atmosphere surrounding the fibers may be the dielectric breakdown of the solvent. Corona parameters such as breakdown voltage and corona current depend on the dielectric properties of the gas medium, notably permittivity. Molecular structure and processes such as molecular excitation, ionization and the specifics of charge carrier interactions have an impact on charge transfer from one ionized molecule to another, which can be expressed in terms of the conduction of the gas surrounding the charged fibers. These chemical alterations may affect the outcome of the electrospinning process in terms of fiber surface modification, fiber diameter distribution, etc. It is clear that solvent evaporation and charge chemistry are major process factors in electrospinning [44].

3. EXPERIMENTAL PART

3.1 Materials

Acrylonitrile (99.5>%) was provided by the Aksa Acrylic Chemistry Company. Itaconic acid (99.5>%) was purchased from Sigma Aldrich. Ammonium persulfate (APS), (99.5>%), dimethylformamide (DMF) and ethanol were all Merck reagents. All these reagents were used without further purification.

3.2 Copolymerization of AN with IA

Copolymer of AN-IA was synthesized by free radical polymerization using APS as an oxidant in the aqueous medium. Copolymerization was carried out in a two necked flask attached a condenser equipped with a stirrer seen in Figure 3.2. 10 g monomer mixture was stirred with distilled water for 30 minutes. 0.3 g APS dissolved in 30 mL distilled water was added to monomer mixture. The ratio of APS to monomers in feed is 3 % (wt). The monomer feed ratios used in this experiments were 99:1, 97:3, 95:5, 93:7 and 91:9 (AN:IA). During copolymerization the temperature was kept at 60 ^{o}C. After 3 hours adding oxidant, copolymerization was finished by stopping heater. The precipitated polymer was obtained in excess ethanol, filtered and dried at 50 ^{o}C under vacuum for 4 hours.

3.3 Electrospinning of P(AN-co-IA) Copolymers

The copolymer solutions were prepared with 5 %wt concentration in DMF at room temperature to produce nanofiber mats. The electrospinning apparatus includes a syringe pump (NE-500 model, New Era Pump Systems, Inc., USA) with feeding rate from 5.5 µL/h to 400 mL/h, high voltage DC power supplier generating positive DC voltage up to 50 kV DC power supply (ES50 model, Gamma High Voltage Inc., USA) and a grounded alumium collector which is covered with aluminum foil. Solution was loaded into a syringe having 12 mm diameter and positive electrode was clipped onto the dispensing needle having 0.8 mm outer diameter. The feeding rate of the polymer solution was controlled by syringe pump and solutions were electrospun horizontally onto the collector. The voltage of power supply was kept 9 – 10 kV. Polymer solution was fed with 1 ml/h flowrate. The flat collector was put 19 cm away from the needle. Figure 3.3 shows the experimental setup of electrospinning process which was used .

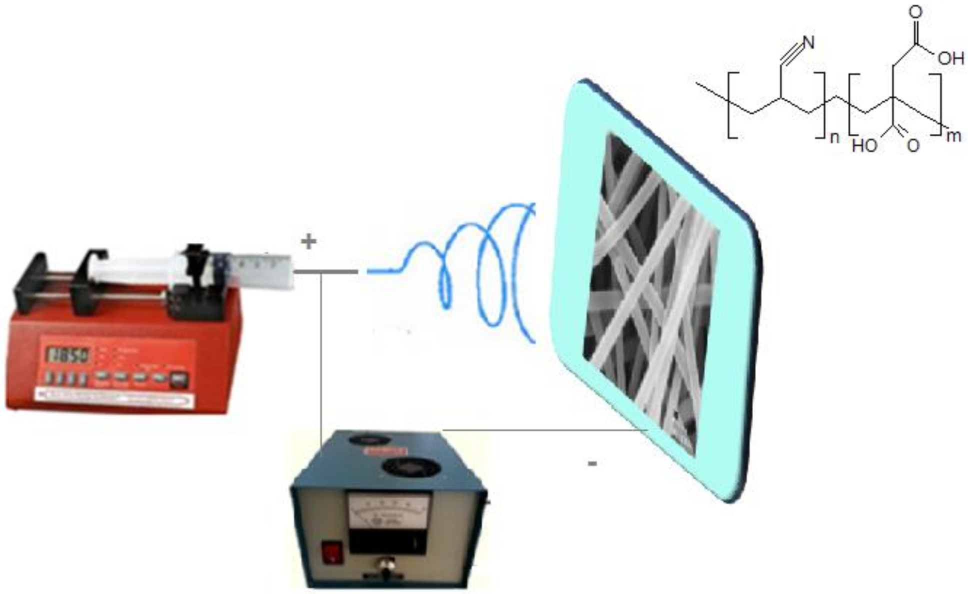


Figure : Experimental setup of electrospinning.

3.4 Stabilization of P(AN-co-IA) Nanofibers

The stabilization was carried out by heating p(AN-co-IA) nanofiber mats from the room temperature to 220 ^{o}C with 1 ^{o}C/min heating rate, followed by holding the temperature at 220 ^{o}C for 14 h to allow the stabilization to complete. The heat treatment performed in a Memmert Ufe 400 oven.

3.5 Characterization

The structure of the copolymers was characterized by means of ^{1}H NMR spectroscopy and Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) spectroscopy. FTIR analysis of P(AN-co-IA) copolymers were performed with FTIR-ATR reflectance spectrophotometer (Perkin Elmer, Spectrum One, with a Universal ATR attachment with a diamond and ZnSe crystal).

^{1}H NMR spectroscopy analysis of AN-IA copolymers was performed using a Agilent VNMRS 500 MHz spectrometer. NMR samples were prepared by dissolving the copolymers in deuterated dimethyl sulfoxide (DMSO-d$_{6}$).

Intrinsic viscosity [η] of the copolymers was measured in dimethylformamide (DMF) solution using an Ubbelohde viscometer in a water bath at 30 ± 1°C.

The DSC and TGA measurements were carried out using Mettler Toledo instruments in Aksa Acrylic Chemical Company laboratuaries. The DSC samples were scanned at a heating rate of 10 °C min^{-1} under air atmosphere from ambient temperature to 400 °C. TGA samples were heated with a heating rate of 10 °C min^{-1} from ambient temperature to 800 ^{o}C under air atmosphere.

DMA measurements of polymer films were performed using TA Q800 instrument by applying multifrequency-strain test method. The film samples were casted from copolymer solutions in DMF to glass surface at room temperature. The casting films were annealed at 80 ^{o}C under vacuum for 24 hours. Tg measurements using DMA run in tension clamps, at a frequency of 1 Hz and a ramp rate of 3°C/min from ambient temperature to 175 ^{o}C.

Morphology of electrospun nanofibers were characterized using Scanning Electron Microscope (Carl Zeiss EVO MA 10) and the samples for the SEM measurements are coated with gold (Ion Sputter Metal Coating Device, MCM-100). The thickness of gold coating was about 30 nm. Diameters of nanofibers were calculated using Adobe Acrobat 9 Pro Extended software.

4. RESULTS AND DISCUSSION

4.1 Copolymer Characterization

The morphology of PAN is unique [17]. Due to strong repellent dipole–dipole interactions between intramolecular neighboring nitrile groups in parallel position, the polymer backbone is forced into an irregular helical conformation. Strong attractive dipole–dipole interactions between antiparallel nitrile groups.

The polymerization of AN is different from the other vinyl polymerization reactions characteristically [19]: AN is soluble in most organic solvents and in water (the azeotrope with water contains 88% of AN). However, PAN is insoluble in most common organic solvents, in water, and in its monomer. For this reason, the polymerization reaction often becomes heterogeneous even at low conversions and monomer concentrations, and the borders between emulsion and suspension polymerization are not well defined. Heterogeneous AN polymerization shows autoacceleration when an insufficient amount of a surfactant is used. Furthermore, there is obviously no consensus among the authors reporting on AN polymerization as far as use of the terms solution polymerization, dispersion polymerization, and precipitation polymerization is concerned, especially in aqueous systems.The results of the copolymerization of AN-IA and feed ratio of monomers as weight and mole percentage for various experiments are listed in Table 1. The conversions of copolymerization calculated gravimetrically are high enough for an effecient polymerization.

Table 4.1: Copolymerization of AN-IA.

	Monomer feed ratio (wt%)		**Monomer feed ratio (mole%)**		**Conversion %***	**[η] (dL/g)**
	IA	**AN**	**IA**	**AN**		
C(IA-1%)	1	99	0.41	99.59	87.8	2,67
C(IA-3%)	3	97	1.25	98.75	65.5	2,41
C(IA-5%)	5	95	2.10	97.90	80.7	1.94
C(IA-7%)	7	93	2.98	97.02	86.5	1,07
C(IA-9%)	9	91	3.88	96.12	83.3	0,92

*Calculated gravimetrically

Based on Devasia's study on viscosity properties, high molecular weight AN-IA copolymers have led to the problem of the rectilinearity of the concentration dependency of reduced viscosity [54]. Viscosity experiments worked using definite concentrations showing rectilinearity, thereby demonstrating the polyelectrolyte behavior caused by ionogenic groups in the copolymer, which at a higher dilution in DMF may undergo greater ionization. For C(IA-%7) reduced viscosity (η_{sp}/C) versus concenration (C) from 1.05 to 0,85 g/dL was plotted and the linear regression line was displayed to obtain intrinsic viscosity in Figure 4.1. The viscosity average molar mass (Mv) of C(IA-7%) was calculated as 7.49x10^5 according to Mark Houwink Sakurada equation [55].

$$[\eta] = 2.86\text{x}10^{-4}M_v^{0.733}$$

Intrinsic viscosity of AN-IA copolymers calculated shows a drop by increasing IA content (Table 4.1). as previously found that the copolymers having higher IA content shows lower intrinsic viscosity [56]. The intrinsic viscosity or the molecular weight of the polymer controls the solid concentration of the dope, the fiber morphology, and the density [57].

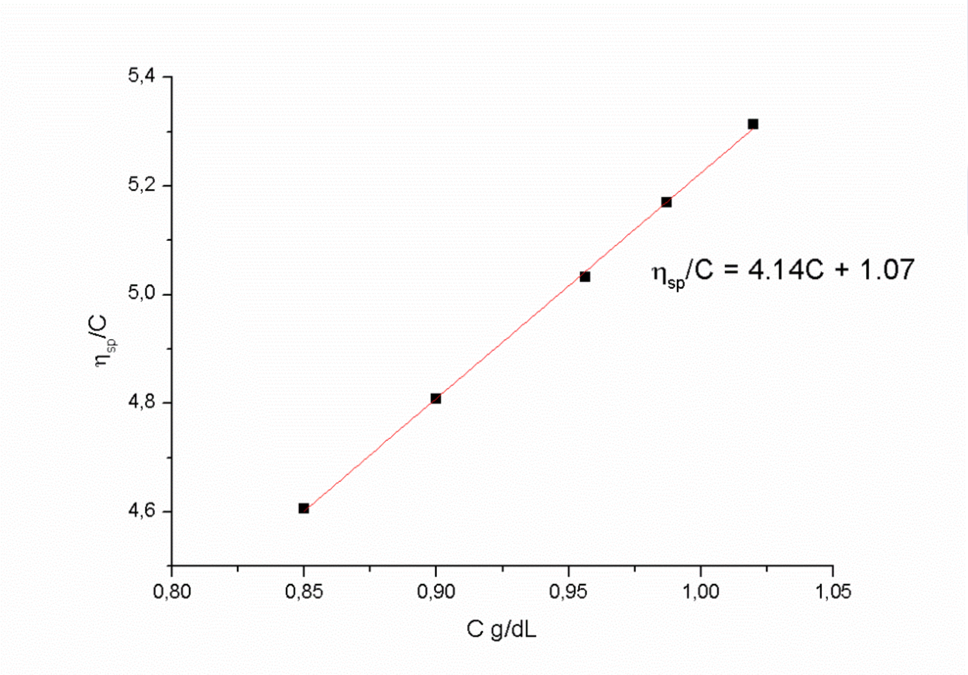


Figure 4.1 : Plot for C(IA-7%) η_{sp}/C versus C in DMF at 30 °C.

4.1.1 FTIR-ATR Spectroscopy

The FTIR-ATR spectra of PAN homopolymer and P(AN-co-IA) copolymer are shown in Figure 4.2 and it was recorded in the absorbance mode. The characteristic peak of C≡N stretching of AN repeating unit is observed as a strong absorption peak at 2244 cm-1 in both PAN and its copolymer. The peak at about 1735 and 1628 cm^{-1} related to the carbonyl stretching vibration of the carboxylic acid was appeared in the spectrum of AN- IA copolymer . The characteristic peak of aliphatic -CH_2- stretching is at 2940 cm-1. There is also a strong band at 1454 cm-1 related to bending vibration of -CH in -CH_2. The band at 1076 cm-1 is ascribed to the -CH bending mode in CH. These results are in agreement with literature [31,58,59].

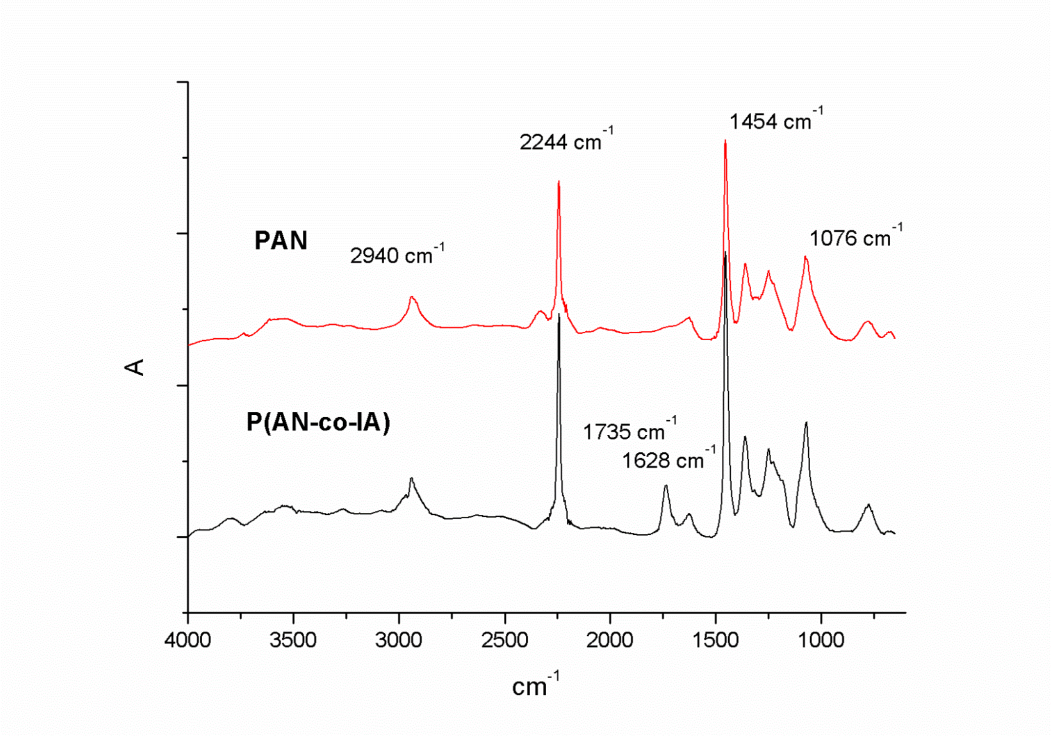


Figure 4.2 : FTIR-ATR spectra of PAN and AN-IA copolymer.

In Figure 4.3 FTIR-ATR spectrums of AN-IA copolymers which synthesized with different proportions of IA were presented in absorbance mode. The peak of carbonyl stretching in copolymers is shifted from 1737 to 1732 cm^{-1}, corresponding to increase in IA feed.

The relation between AN and IA units in copolymers composition was founded by comparing the strong bands at 2244 cm^{-1} due to C≡N stretching vibration and 1628 and 1730 cm^{-1} due to C=O stretching vibrations. Absorbance ratio of the characteristic peaks of carboxylic acid to C≡N stretching vibration of AN units was plotted versus IA feed ratios (wt%) in Figure 4.4. The absorbance ratios shows an increasing trend in copolymers which had feeded high IA.

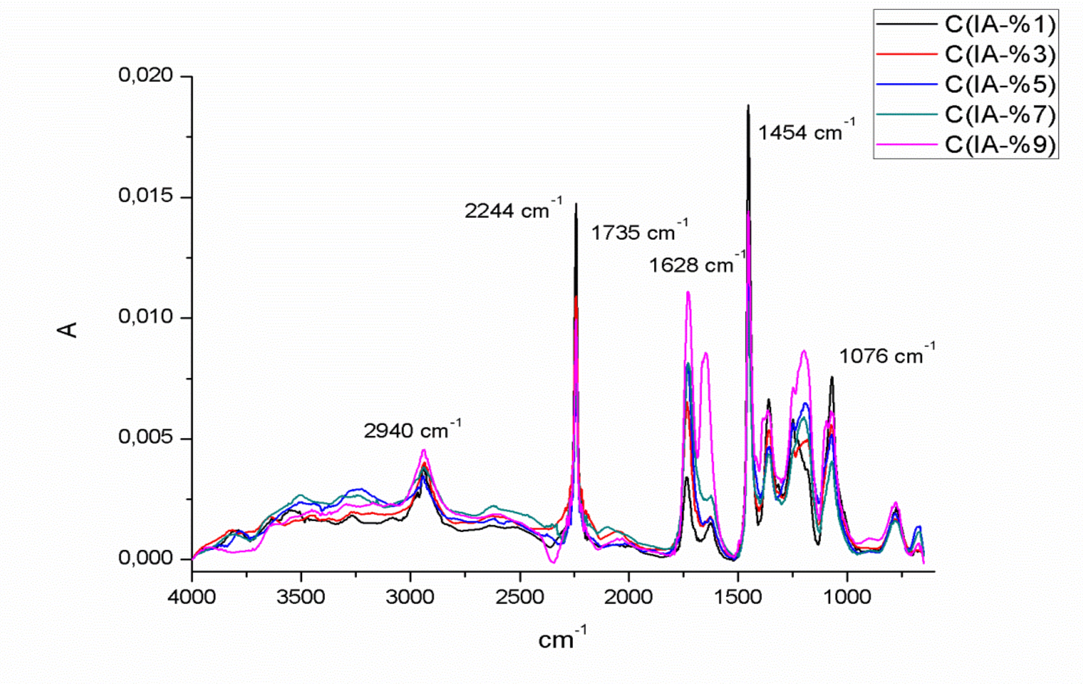


Figure 4.3 : FTIR-ATR spectras of AN-IA copolymers

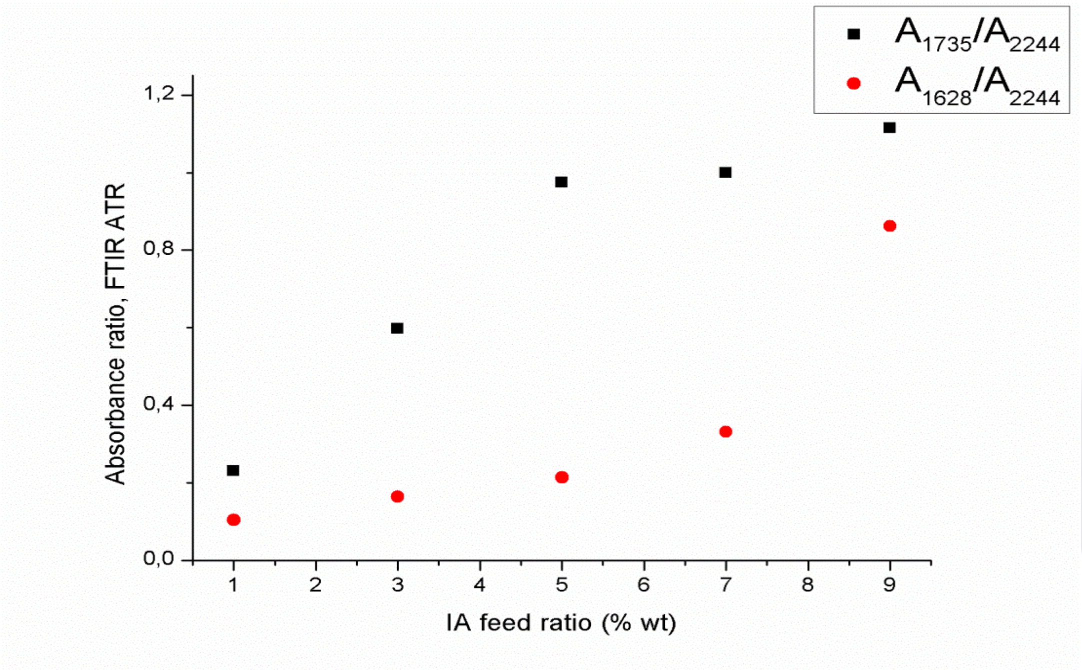


Figure 4.4 : The relation between the absorbance ratios and the initial feed ratio of AN-IA copolymers based on the FTIR-ATR results

4.1.2 Nuclear magnetic resonance (NMR) spectroscopy

^{1}H NMR are used to specify the composition of AN-IA copolymers which is shown as chemical structure in Figure 4.5. ^{1}H NMR spectrum of AN-IA copolymer coded C(IA-1%) is seen in Figure 4.6. The signal at 2.2 – 1.85 ppm is related to -CH_2 protons of both AN and IA (a). The signals of -CH proton of AN (b) were observed at 3.25 – 3.09 ppm. The other peaks seen in the ^{1}H-NMR spectrum are related to solvent, DMSO-d_6. NMR results are in agreement with literature [58].

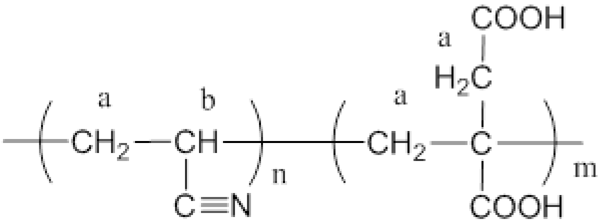


Figure 4.5 : Chemical structure of AN-IA copolymer indicated protons.

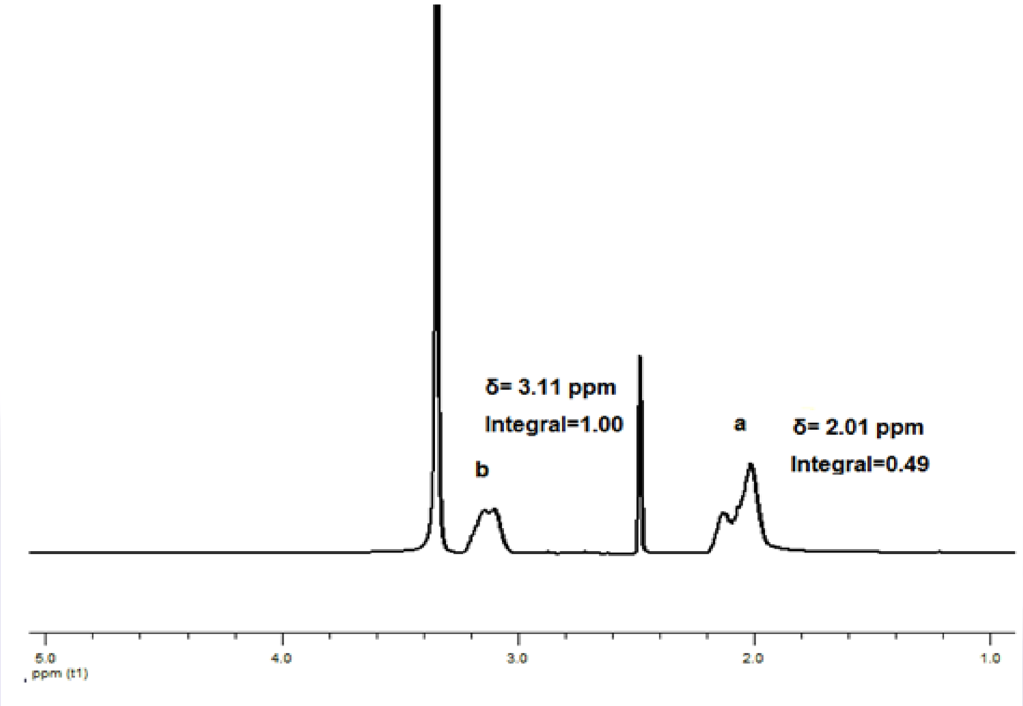


Figure 4.6 : ^{1}H NMR spectrum of AN-IA copolymer coded C(IA-1%).

The copolymer compositions calculated from the ratio of the integrals of the peaks related to a and b protons. IA content in the copolymers as molar percentage and also absorbance ratios determined from FTIR ATR spectrums are listed in Table 4.2. High IA content of copolymers can be explained by reactivity ratios that r_{IA}=1.37 is higher than r_{AN}= 0.64 [35].

Table 4.2 : Determination of copolymer compostion.

	IA feed ratio (mole%)	**IA content (mole %)***	**Absorbance ratio****
C(IA-1%)	0.41	1.00	0.23
C(IA-3%)	1.25	1.92	0.60
C(IA-5%)	2.10	2.23	0.97
C(IA-7%)	2.98	3.14	0.99
C(IA-9%)	3.88	4.09	1.11

*Calculated from NMR spectrums

** Determined from FTIR ATR spectrums A_{1735}/A_{2244}

NMR spectroscopy is a certain way to determine copolymer compositions, but it is time consuming because of sample preparation. Copolymer characterization by FTIR spectroscopy, especially in ATR mode is a very practical way. Therefore, a calibration curve was fitted using FTIR ATR absorbance ratios and IA content (% mole) calculated from NMR results (Figure 4.7).

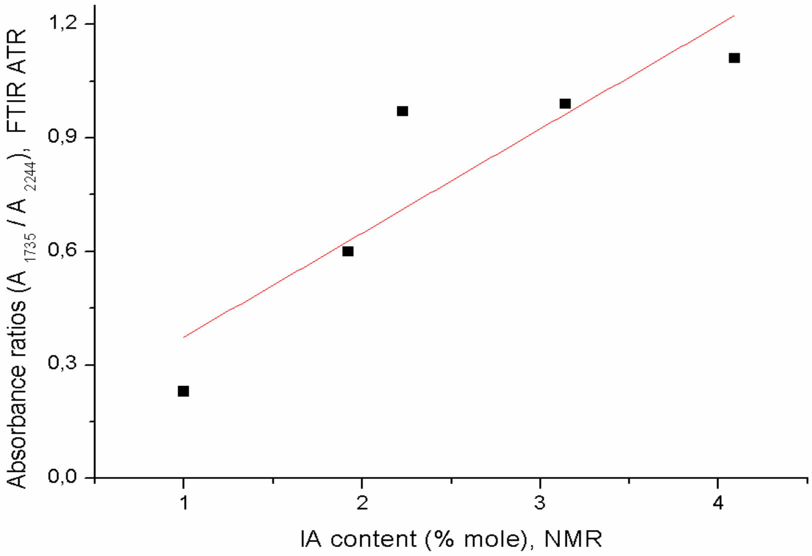


Figure 4.7 : Calibration curve fitted based on absorbance ratios and IA content (% mole) calculated from NMR results

4.1.3 Differential scanning calorimetry (DSC)

The DSC curves of AN-IA copolymers all show a doublet exothermic peak between 200 and 300 °C (Figure 4.8). Based on the DSC studies, PAN homopolymer exhibits a single sharp peak centered at 310 °C which is known that it is related the cyclization reactions in the PAN homopolymer following a free radical mechanism at high temperature. Carboxylic acid groups in AN-IA copolymers can initiate the cyclization reactions at a lower temperature through an ionic mechanism [60]. First exothermic peak at the lower temperature is associated with the ionic cyclization reactions which are described in Figure 4.8. As for C(IA-1%), it appears as a shoulder at about 222 °C. With IA content increasing, initiation temperature (T_i) decreases from 222 to 195 °C.

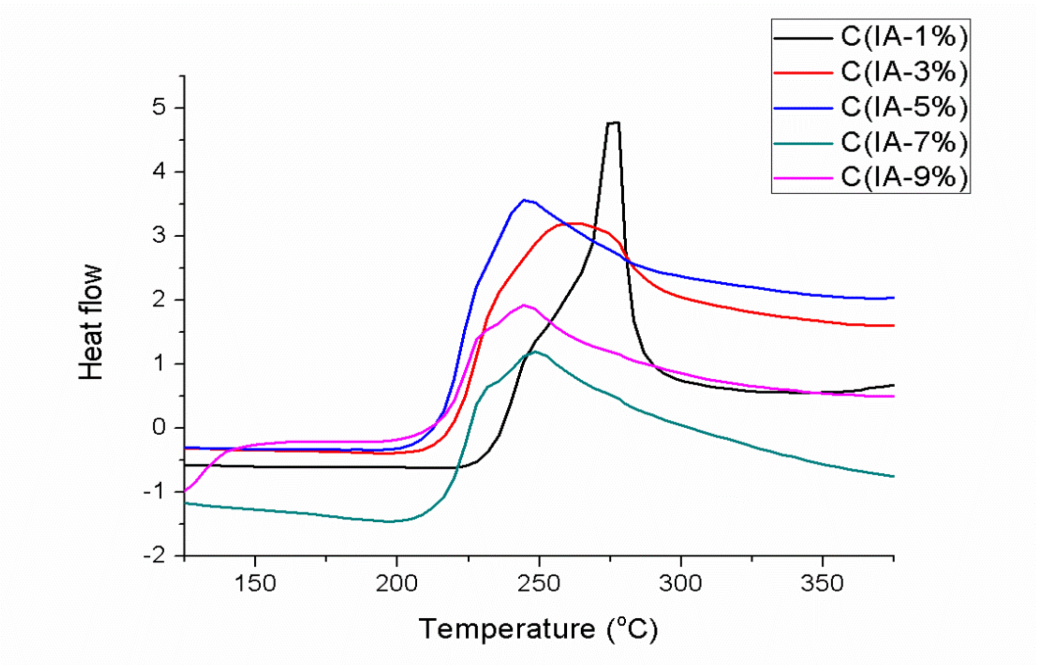


Figure 4.8 : DSC curves of AN-IA copolymers with different IA contents at a heating rate of 10°C min^{-1}

The ionic cyclization reactions are initiated by elimination of hydrogen ion (Figure 4.9). The hydroxyl oxygen of –COOH in IA units has made a nucleophilic attack on the carbon atom of neighbour nitrile group and induce it to cyclize. Cyclization reactions lead to the development of ladder structures by oligomerization of nitrile (C≡N) groups. Oligomerization is terminated by addition of hydrogen ion [61].

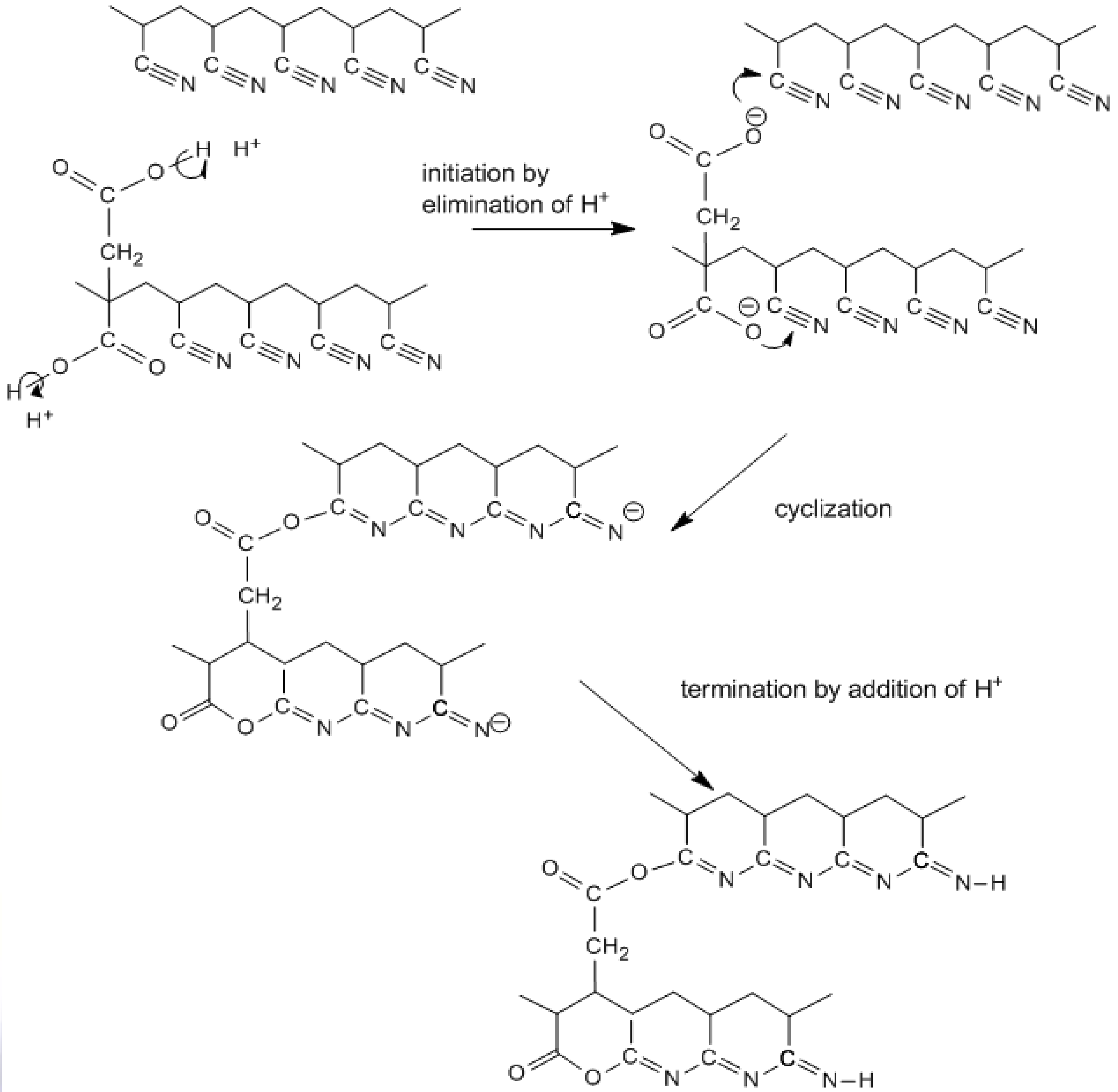


Figure 4.9 : Cyclization mechanism of AN-IA copolymers

[61], the first exothermic peak at the lower temperature side is assigned to cyclization reactions including hydrogenation and oxidation, and the second peak is attributed to the secondary oxidative reactions. Summary of stabilization parameters obtained from DSC exoterms is presented in Table 4.3. All the stabilization parameters shows a significant decrement, which implies IA is effective to control the exothermic behavior and improve the stabilization treatment. The relation between stabilization parameters and IA feed ratio (wt%) is shown in Figure 4.10.

Table 4.3 : Summary of stabilization parameters obtained from DSC exoterms.

Sample	T_i (°C)	$T_{peak\ 1}$ (°C)	$T_{peak\ 2}$ (°C)
C(IA-%1)	222.8	249.6	276.6
C(IA-%3)	204.3	236.4	257.9
C(IA-%5)	199.3	227.9	245.8
C(IA-%7)	198.2	231.4	247.1
C(IA-%9)	195.5	227.6	246.3

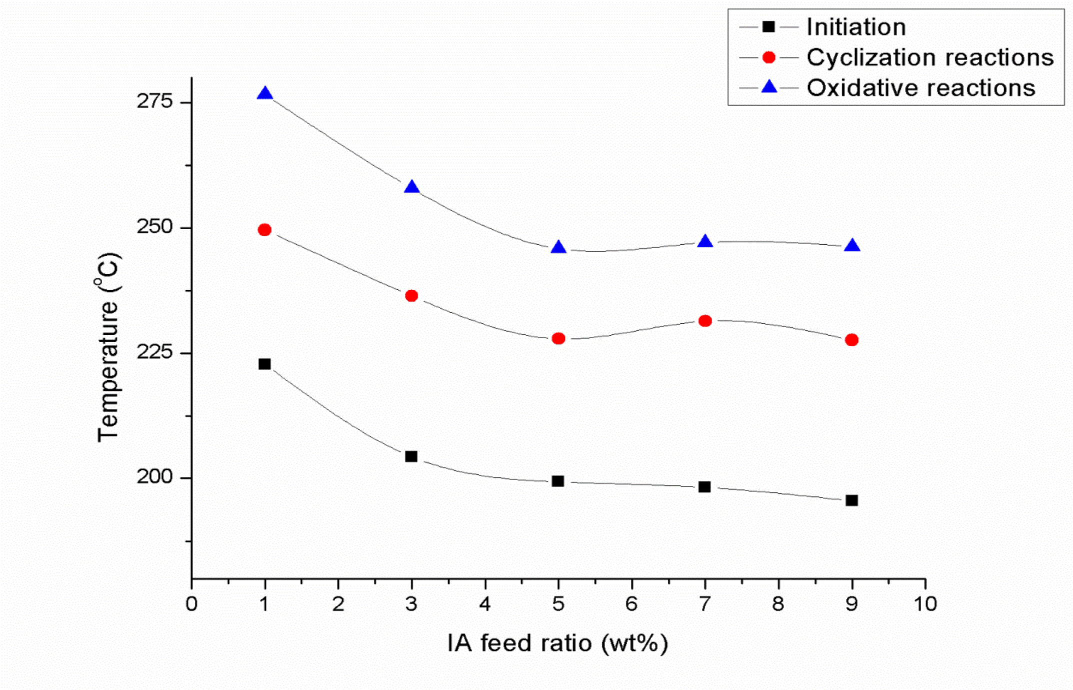


Figure 4.10: Relation between stabilization parameters and IA feed ratio (wt%).

4.1.4 Thermal gravimetric analysis (TGA)

Grassie and McGuchan showed the strong initiating effect of acrylic, methacrylic, and itaconic acid and acrylamide on the exothermic nitrile group oligomerization [32]. As the acid content increases, the DSC exotherm becomes less intense and broader with lower initiation and peak temperature. The methacrylic and itaconic acid copolymers show more complex and broad exotherms than the AN-AA copolymer. In N2 atmosphere, the initiation temperatures 220, 200 and 190 oC were found for AN-AA, AN-MAA and AN-IA copolymers respectively. Among these acidic monomers IA improves thermal process most effectively.

In PAN the cyclization of nitrile groups only can be initiated at a higher temperature through a free radical mechanism, while in P(AN-co-IA) the cyclization can be initiated by the carboxylic groups of IA units at a lower temperature through an ionic mechanism Figure 2.1 [33]. As shown in second reaction, the hydroxyl oxygen of –COOH in IA unit has made a nucleophilic attack on the carbon atom of an adjacent nitrile group and induced it to cyclize. The major reason for the superiority of IA over other acidic comonomers is the presence of two carboxylic groups, which provides more opportunities to induce the nitrile group to cyclize following the ionic mechanism.

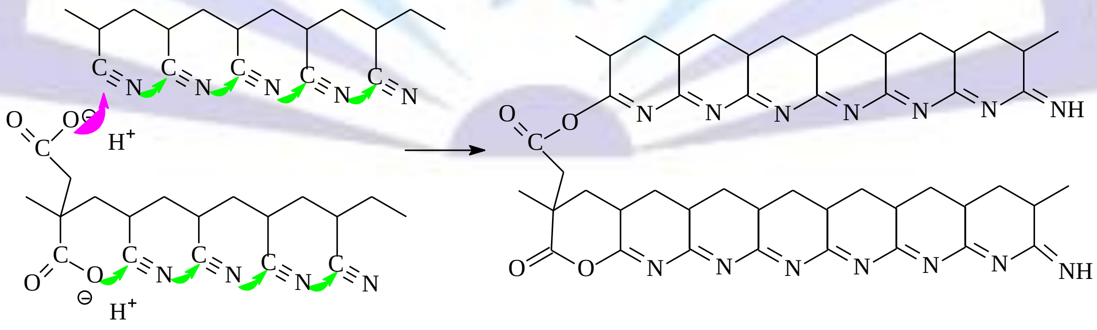


Figure 2.2 : Cyclization in AN-IA copolymer initiated through an ionic mechanism [33].

The effect of itaconic acid as a comonomer and additive on the exothermic reaction of acrylonitrile copolymers has been studied by Tsai et al [34]. As the itaconic acid content increases from 0.5 to 3.5 mol % in the copolymer, the exothermic peak becomes complex with several distinct maxima. Further, the initiation of nitrile oligomerization was also confirmed with itaconic acid as an additive. The rate of cyclization, however, would depend on the sequence distribution of the comonomer in the acrylonitrile copolymers.

The thermal behaviour of AN-IA copolymers with varying IA content were compared under air atmosphere at a heating rate of 10 °C min^{-1} shown in Figure 4.11. The weight loss seems to be divided into two steps basically [62]. The first step is starting at about 230 - 250 °C which may be mainly due to the dehydrogenation and carboxylation reactions presented in Figure 4.12, because the nitrile cyclization reactions theoretically do not cause any weight loss.

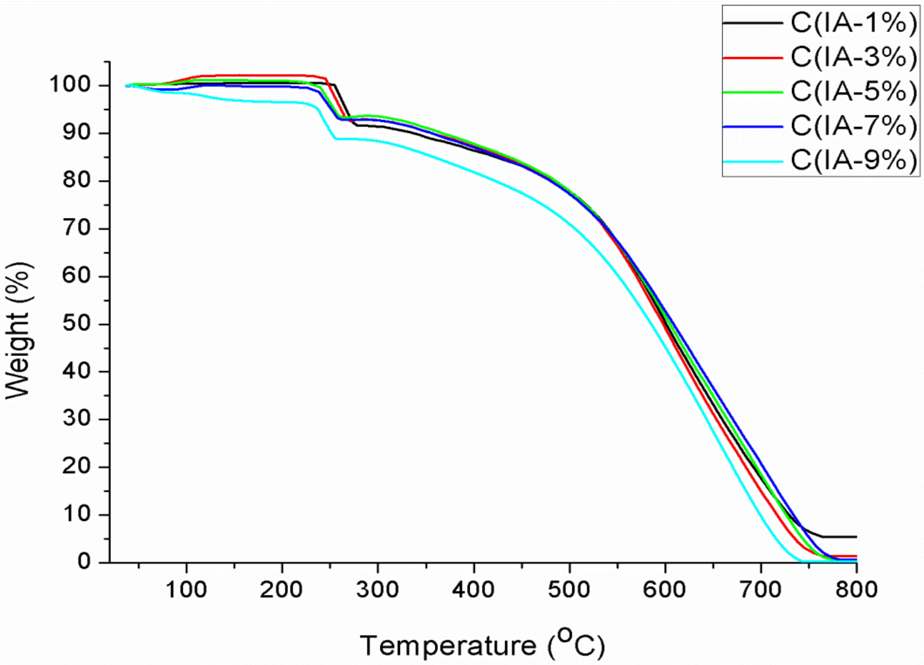


Figure 4.11: TG curves of AN-IA copolymers under air atmosphere at a heating rate of 5 °C min^{-1}.

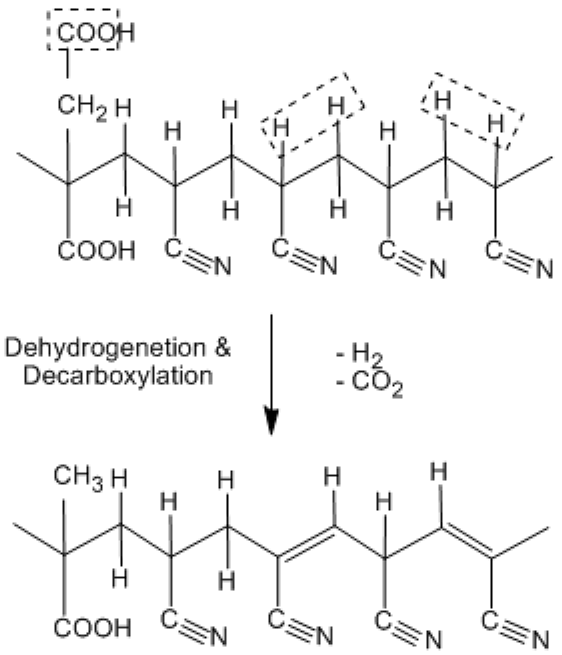


Figure 4.12: Dehyrdrogenetion and de carboxylation reactions.

However, the rate of weight loss in the second step is quiet large, which could be attributed to the occurrence of oxidative reactions, causing fragmentation of polymer chains and evolution of gas fragments such as HCN, NH_3,CO_2, H_2O [63]. The starting temperature of second step can be assumed as decomposition temperature between 277 and 257 °C.

Ionic cyclization occurring at low temperature improves stabilization, but IA also causes to decrease in decomposition temperature (T_d). The difference between T_d obtained from TGA and T_i obtained from DSC is listed in Table 4.4 and plotted in Figure 4.13. For C(IA-1%) copolymer, the temperature difference is lowest. Higher IA content is useful for prevent decomposition during cyclization, although the copolymers with higher IA content have low decomposition temperature.

Table 4.4 : Thermal decomposition temperature of AN-IA copolymers.

Sample	T_{step1}	T_d	T_d-T_i
C(IA-%1)	254.2	277.8	55
C(IA-%3)	245.2	268.8	64.8
C(IA-%5)	239.8	262.5	63.2
C(IA-%7)	238.1	262.1	63.9
C(IA-%9)	232.7	257.7	62.2

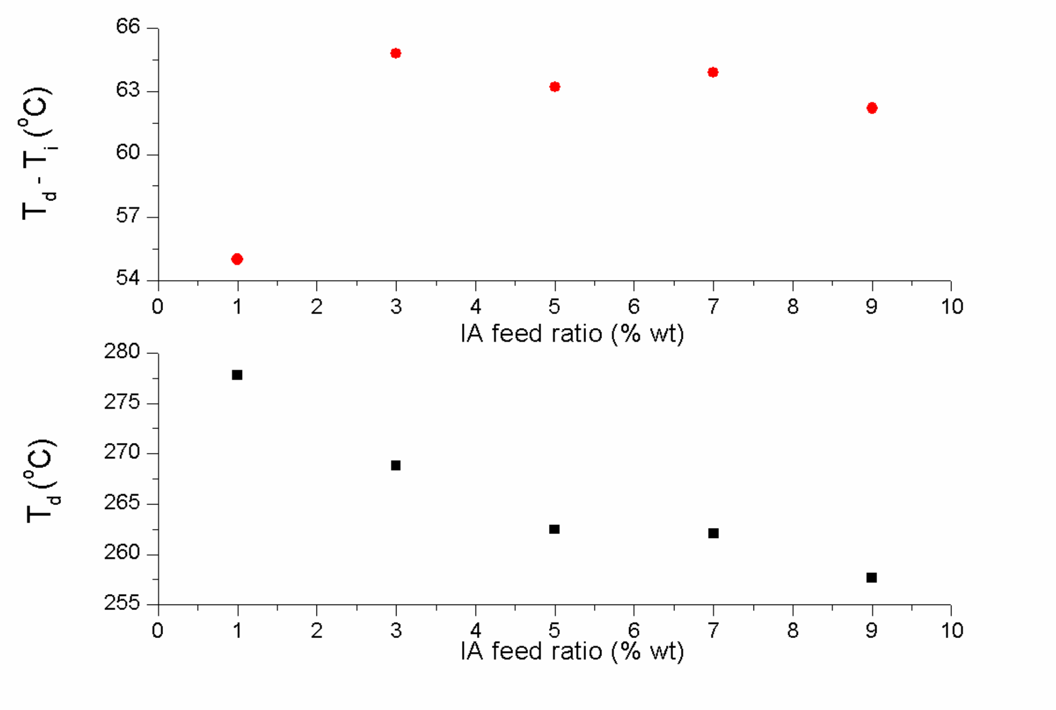


Figure 4.13 : The relation between T_d and T_d-T_i with IA feed ratio (% wt).

4.1.5 Dynamic mechanical analysis (DMA)

The determination of Tg using differential scanning calorimetre has been difficult due to the strong exothermic reaction, minor transitions like Tg cannot be seen [62]. The Tg of AN-IA copolymers was obtained from the temperature corresponding to the maximum of the tan delta curves determined with multifrequency – strain test method (Figure 4.14) using DMA instrument. In this test method, storage modulus (E') and loss modulus (E'') are measured by applying heat and force at a frequency to the film samples. Storage and loss modulus are elastic and viscous response of material respectively. The ratio of E''/E'is called damping factor (tan delta). Tg values of the copolymers decreases, with increasing IA content, while tan delta increases (Table 4.5). The Tg and damping factor of copolymers shows an increasing trend, by increasing the amount of IA adding the copolymer. IA comonomer which is crystalline with a melting point 167-168 ^{o}C [64], cannot cause an softening effect on PAN naturally.

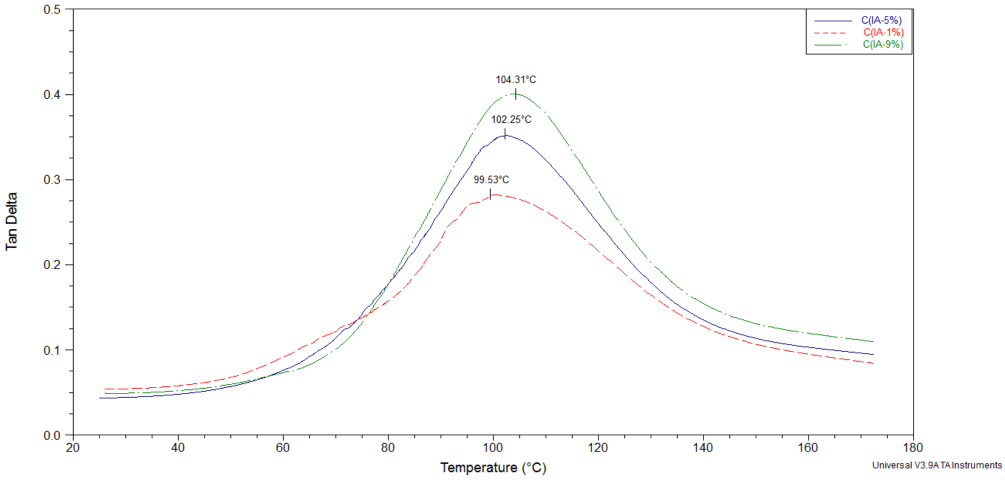


Figure 4.14 : Tan delta curves of AN-IA copolymers; C(IA-1%), C(IA-5%) and C(IA-9%).

Table 4.5 : DMA results of AN-IA copolymers.

Sample	T_g (^oC)	Tan delta
C(IA-%1)	99.53	0.28
C(IA-%5)	102.25	0.35
C(IA-%9)	104.31	0.40

4.2 Morphology of Elecrospun Nanofibers

Electrospinning solutions were prepared from AN-IA copolymers having different itaconic acid content in DMF. All the solutions had same concentration (5 wt%). Electrospinning parameters (distance and flowrate) were also kept constant. Required minumun voltage to create spinning jet was applied to the solution, for the C(IA-1%) solution it was 10.5 kV and 9 kV was enough for the other solutions. The effect of itaconic acid on nanofiber diameters was investigated in this part of study. In Figure 4.15 and 4.16, SEM images of electrospun nanofibers with 20,000 magnitude are seen. Based on the SEM images, bead free nanofibers were produced from all the copolymer solutions.

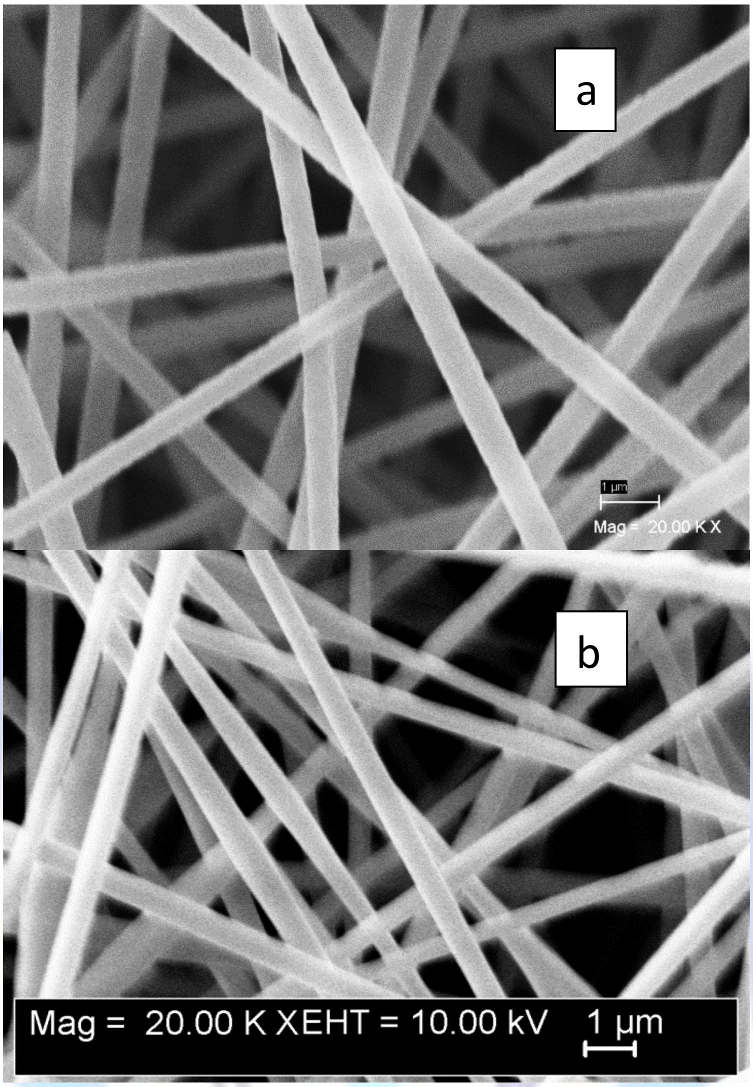


Figure 4.15 : SEM images of electrospun nanofibers with 20,000 magnitute; (a) C(IA-1%), (b) C(IA-3%).

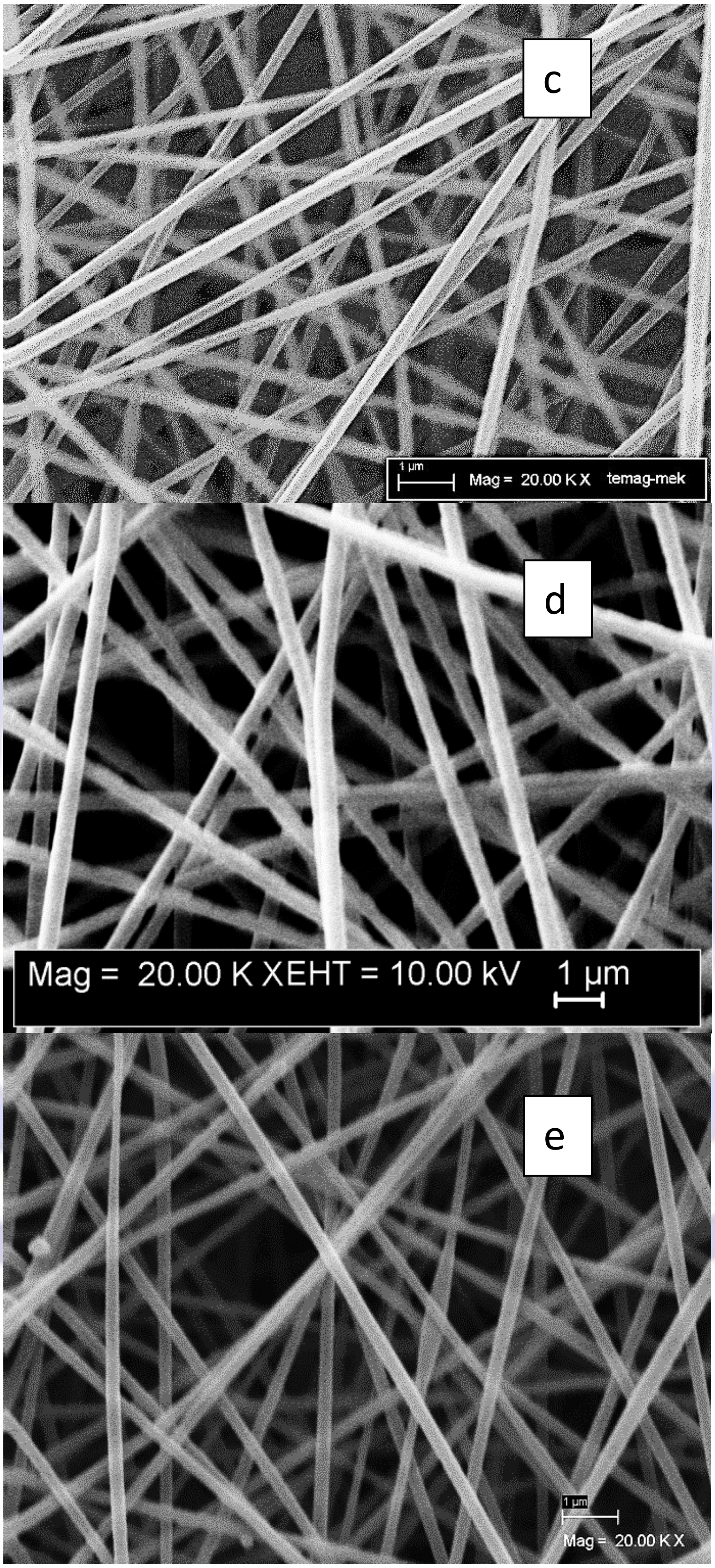


Figure 4.16 : SEM images of electrospun nanofibers with 20,000 magnitute; (c) C(IA-5%), (d) C(IA-7%) and (e) C(IA-9%).

About 20 nanofiber was measured from the SEM images of nanofiber mats with x20,000 magnitute to obtain average nanofiber diameter which was presented as box plot in Figure 4.17. C(IA-1%) sample which has the lowest IA content exhibited the highest average nanofiber diameter, 878±18 nm. The average nanofiber diameter decreases corresponding with IA content in copolymers. Decrement in standart deviation of nanofibers shows that uniformity of nanofibers is improved by increasing IA content.

Table 4.6 : Nanofiber diameters obtained from SEM images.

Sample	Ave. nanofiber diameter (nm)	Standart deviation (nm)
C(IA-%1)	878	18
C(IA-%3)	747	24
C(IA-%5)	704	13
C(IA-%7)	508	10
C(IA-%9)	386	7

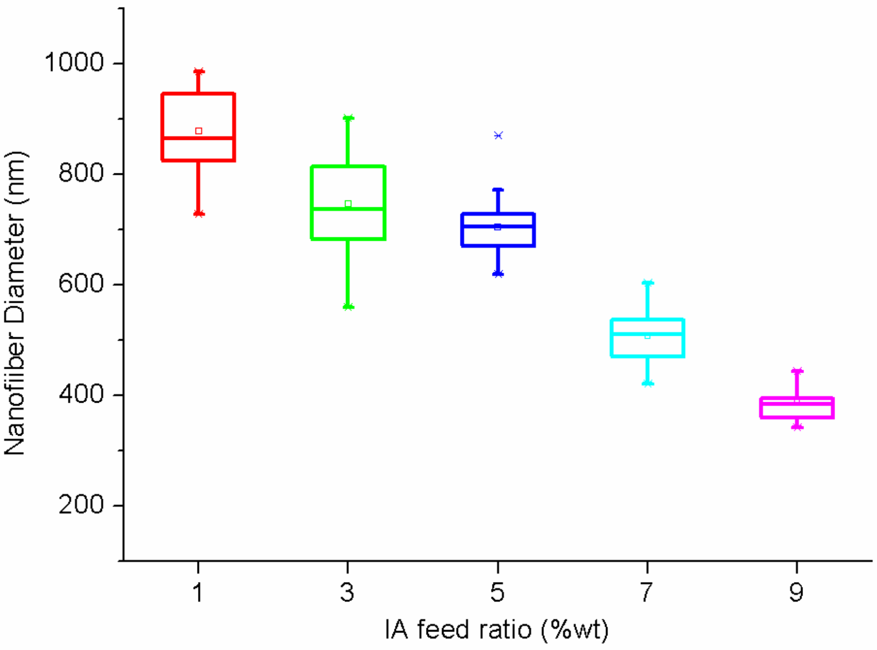


Figure 4.17 : Nanofiber diameter range for AN-IA copolymer.

The nanofibers transport charge across the distance between the charged needle and the grounded collector in electrospinning process. During the electrospinning process the electric current due to ionic conduction of charge in the polymer solution is so small that is considered negligible [44], so the only mechanism of charge transport is the flow of polymer from the syringe to the collector plate. Thus, an increase in the IA contents of copolymers might reflect an increase in the electrospinning current from the capillary tip to the grounded target when all other variables are held constant.

The intrinsic viscosity of AN-IA copolymers are varied from 2.67 to 0.92 dL/g. Electrospun nanofibers prepared from the solutions having same solid concentration exhibit nanofiber diameters paralel to the decrement in the intrinsic viscosities. The relation betweeen nanofiber diameters and intrinsic viscosities are shown in Figure 17. In our previous study, the effect of vinyl acetate content of AN-VAc copolymers on nanofiber diameters has been investigated. Increasing VAc content of copolymers resulted in decreasing nanofiber diameter which is related to low intrinsic viscosity [65].

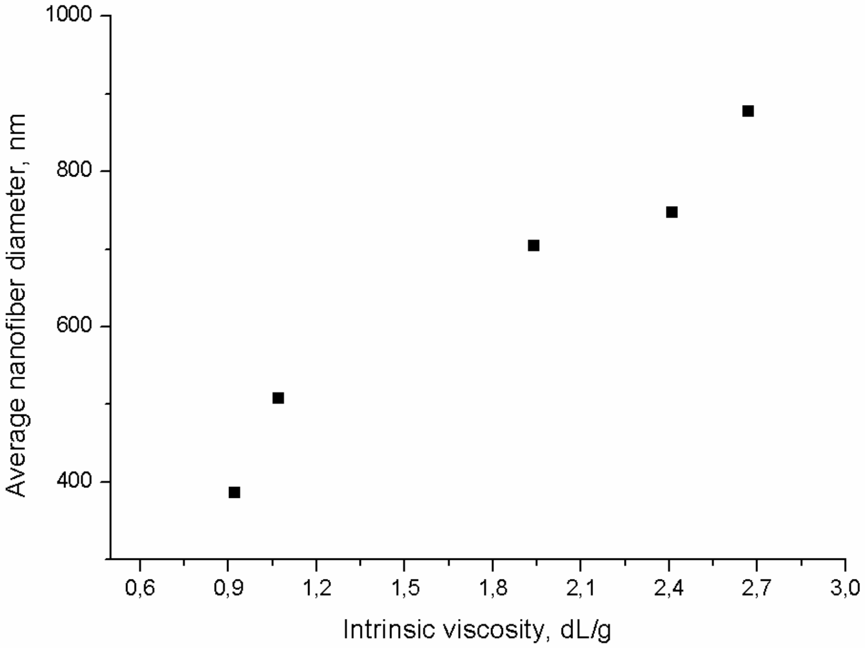


Figure 4.18 : Relation between nanofiber diameter and intrinsic viscosity.

4.3 Characterization of Stabilized Nanofibers

Electrospun nanofibers of AN-IA copolymers were treated with heat at 220 ^{o}C under air atmosphere to investigate physical and chemical changes occuring on the copolymers. The main reason for choosing 220 ^{o}C as the final temperature for stabilization is DSC results showing that the initiation reactions start at about 220 ^{o}C.

The first observation is that the color of nanofiber mats turned to brown-red from white visibly after the heat treatment. The mechanism of coloration is not fully understood, but the different shades of brown-red seen in stabilized nanofiber mats can imply variation in conjugation degree between AN-IA copolymers. The photograph of stabilized nanofiber mats is shown in Figure 4.19.

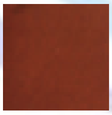
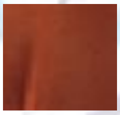
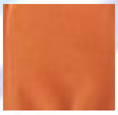
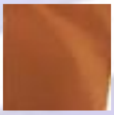
Sample	C(IA-1%)	C(IA-3%)	C(IA-5%)	C(IA-7%)	C(IA-9%)
Color of stabilized nanofiber					

Figure 4.19 : The photograph of stabilized nanofiber mats.

4.3.1 FTIR-ATR Analysis of stabilizied nanofibers

FTIR analysis of stabilized nanofibers of AN-IA copolymers shows that the strong CN stretching band at 2243 cm^{-1} shown in precursor fully disappeared after stabilization process (Figure 4.20). CN band centered at the wavenumber of 1585 cm^{-1} and C-H band in the =CH- structure centered at the wavenumber of 1370 cm^{-1} had significantly high intensities. This indicates the formation of cyclic conjugation leading to a tetrahydropyridine-type ladder structure, as shown in Figure 4.8. Additionally, the emerging band centered at the wavenumber of 805 cm^{-1} indicated that aromatic structures started to form in the stabilized P(AN-co-IA) nanofibers and this band was attributed to the vibration motion of C-H bond in aromatic structures. The observed FTIR bands in stabilized copolymers agree with previous workers approximately[31].

It was reported that the cyclization of PAN macromolecules could be initiated by the functional groups of carboxyl and/or hydroxyl through the reduction of activation energy for the reaction [60]. IA units in the precursor of electrospun nanofibers could effectively initiate the cyclization and further induce the aromatization, as and this was evidenced by the FTIR ATR. The well-stabilized PAN nanofibers possessed regularly oriented ladder structures, which can further facilitate the formation of ordered graphitic structures in carbon nanofiber. [12].

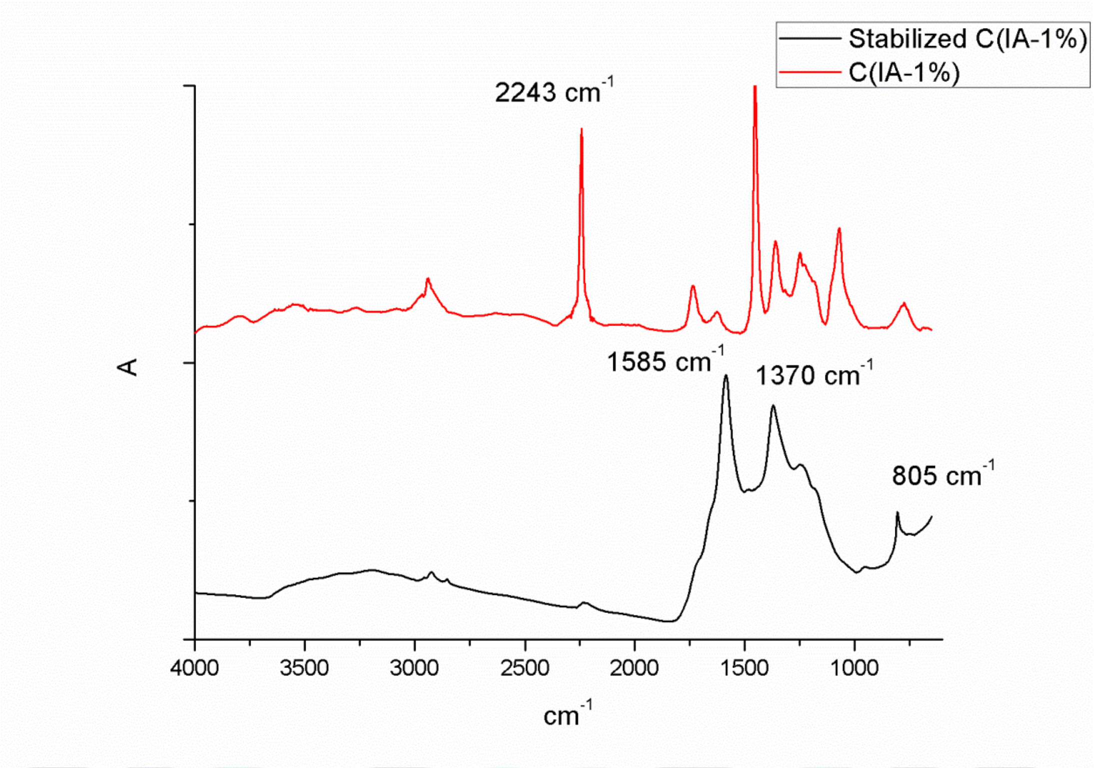


Figure 4.20 : FTIR-ATR spectrum of stabilized C(IA-1%) and its precursor.

4.3.2 Morphology of stabilized nanofibers

SEM images of nanofibers of C(IA-5%) copolymer before and after heat treatment are seen in Figure 4.21. Obviously, diameters of nanofibers decreased as a result of reactions and thermal decomposition during heating process. If it is assumed that nanofibers are cylindrical and volume loss occurs homogeneously, volume loss percentage can be correlated with the difference between squared nanofiber diameters before and after heat treatment.

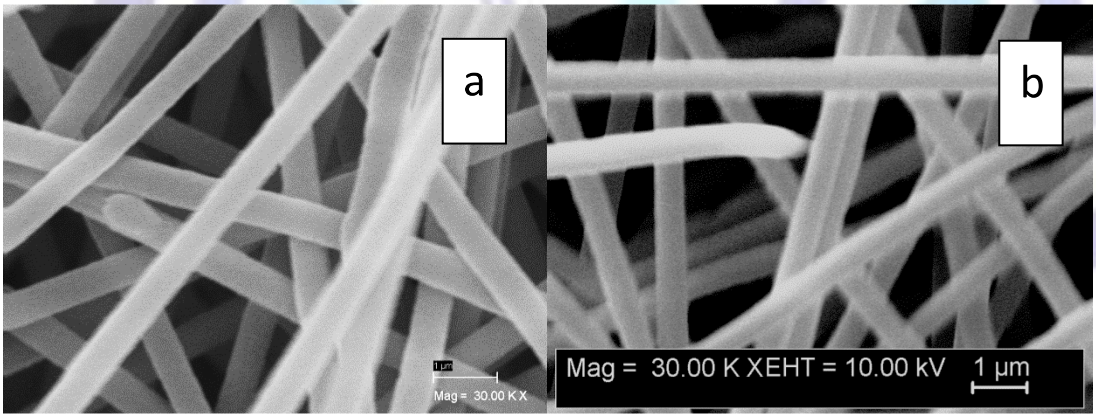


Figure 4.21 : SEM images with 30,000 magnitute; (a) C(IA-5%) precursor, (b) Stabilized C(IA-5%) nanofibers

SEM images of the other stabilized nanofibers were shown in Figure 4.21. The average nanofiber diameter was obtained measuring about 20 nanofiber from the SEM images with x20,000 magnitute. Volume loss (%) calculated and average nanofiber diameter were presented in Table 4.7. Volume loss for the nanofibers produced from the copolymer having the fewest IA content is highest, 48,7. The other stabilized nanofibers had a volume loss between 31.3 and 21.3, it can imply the copolymers produced feeding IA more than 3 % (wt) is more effective in stabilization without volume loss.

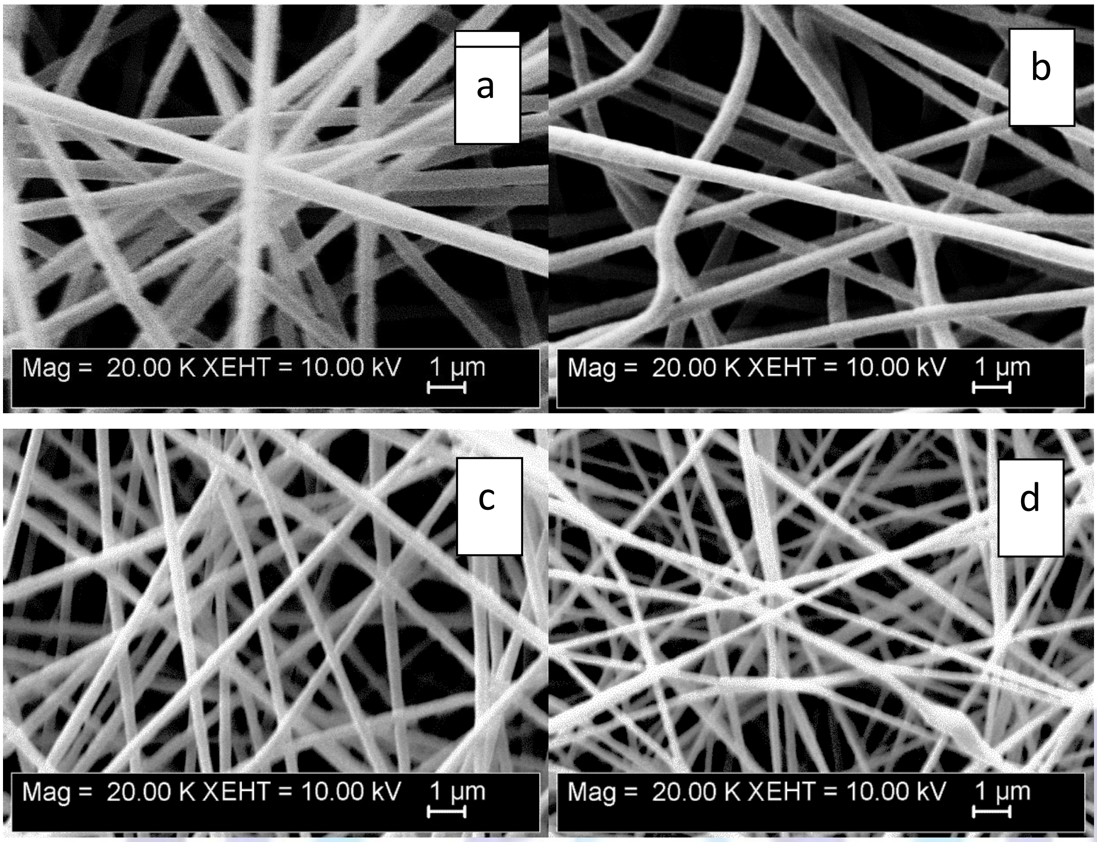


Figure 4.22 : SEM images with x 20,000 magnitute of stabilized nanofibers; (a) C(IA-1%), (b) C(IA-3%), (c) C(IA-7%) and (d) C(IA-9%).

Table 4.7 : The diameters of stabilized nanofibers

Sample	Ave. nanofiber diameter (nm)	Volume loss %
C(IA-%1)	629±13	48.7
C(IA-%3)	619±9	31.3
C(IA-%5)	738±11	21.3
C(IA-%7)	434±7	27.0
C(IA-%9)	341±6	21.9

5. CONCLUSION

AN-IA copolymers were sythesized in aqueous medium changing the monomer feed ratios. Copolymerizations were achieved with high conversion owing to water-phase precipitation polymerization. Increasing IA concentration in copolymerization results in lower viscosity. IA content of copolymers were determined using FTIR ATR and NMR spectroscopies. The absoption bands at 1628 and 1730 cm-1 due to C=O stretching vibrations in carboxylic acid showed an increase comparing to the characteristic peaks of to C≡N stretching vibration of AN in copolymers which had feeded higher IA. ^{1}H-NMR results also supports AN-IA compositions in copolymers.

IA content confirmed by spectroscopic analysis seriously affects thermal properties which is important for carbon nanofiber production. Based on the DSC studies, IA provides an catalytic effect on stabilization process by decreasing initiation cyclization reaction temperature from 202 to 195 ^{o}C. Oxidative reactions are also decreased because of increasing acid content. TG analysis shows two reactions based on weight loss. Thermal decomposition reactions relasing HCN, NH_3,CO_2, H_2O gases starts at second step. The copolymers having high IA content shows decomposition at lower temperatures. DMA was used to determine Tg values appling force and heat to the casting films. IA comonomer having crystalline structure couldn't shows an improving effect on segmental mobility of macromolecule chains, Tg values increases.

Elecrospinning from the AN-IA copolymer solutions in dimethyl foramide (DMF) was performed and Morphology of nanofibers was monitored using SEM. Bead free nanofibers were produced from AN-IA copolymer solutions under same conditions. Average nanofiber diameter decreases from 878±18 to 376±7 nm according to increasing IA content in copolymers.

The nanofiber mats produced were treated at high temperature under air atmosphere to investigate physical and chemical changes occurring on the copolymers. The color of nanofiber mats turned to different shades of brown-red from white visibly after the heat treatment. It degree between AN-IA copolymers. Stabilized nanofibers were characterized using FTIR-ATR spectrometer and a new structure was monitored as a result of cyclization reactions. The stabilized nanofibers were also characterized morphologically using SEM. Volume loss occurring after heat treatment calculated based on the nanofiber diameter changes. The nanofibers produced from the copolymer having the smallest IA content showed highest volume loss, 48,7 %. The other stabilized nanofibers had less volume loss, it can imply the copolymers produced feeding IA higher than is more effective in stabilization without volume loss. These results also can be associated with the results obtained from thermal analysis. According to DSC and TGA results the copolymers were synthesized with IA feed higher than 1 % (wt) have to show good stabilization performance.

Consequently, electrospun nanofibers of AN-IA copolymers can be suggested as a carbon nanofiber precursor due to suitability for electrospinning and stabilization process.

Conductive nanofibrous membranes are quite suitable for use as porous electrodes in developing high performance batteries and polymer electrolyte membrane fuel cells (PEMFCs) due to its high porosity and inherent large total surface area. Polymer batteries have been developed for cellular phones to replace conventional, bulky lithium batteries. The components of polymer batteries are a carbon anode, a lithium cobalt oxide cathode, and a polymer gel electrolyte. Conductive nanofibers offer noteworthy properties of polymer batteries, for example, less electrolyte leakage, high dimension flexibility, and high energy density per weight [51]. there is still a need to improve energy density per weight of polymer batteries to increase their use.

Recently, carbon nanofiber webs have been prepared [52,53] through the electrospinning technique and evaluated on the application of these materials in electrical energy-storage systems. methodologies to develop carbon nanofiber webs as a novel electrode material for electric double layer supercapacitor showing high performance by increasing spesific surface area are important .

.REFERENCES

[1] Bajaj, P., Paliwal, D. K., Gupta, A. K. Acrylonitrile–acrylic acids copolymers. I. Synthesis and characterization, *Journal of Applied Polymer Science*, 49(1993)823–833

[2] Han, N., Zhang, X., Wang, X., Ning Wang, N. . Fabrication, structures and properties of Acrylonitrile/Vinyl acetate copolymers and copolymers containing microencapsulated phase change materials, *Macromolecular Research,* 18(2010)144-152,

[3] Bhanu, V.A., Rangarajan, P., Wiles, K., Bortner, M., Sankarpandian, M., Godshall, D., Glass, T.E., Banthia, A.K., Yang, J., Wilkes, G., Baird, D., McGrath. J.E., . Synthesis and characterization of acrylonitrile methyl acrylate statistical copolymers as melt processable carbon fiber precursors, *Polymer*, 43 (2002)4841–4850,

[4] Han, N., Zhang, X., and Wang, X.C., Various Comonomers in Acrylonitrile Based Copolymers: Effects on Thermal Behaviour., *Iranian Polymer Journal,* 19 (2010) 243-253

[5] Gupta, K., Paliwal, D. K., Bajaj, P. Acrylic Precursors for Carbon Fibers. *Journal of Macromolecular Science. Part C: Polymer Reviews*, 31(1991) 1-89

[6] Yu, M., Wang, C., Zhao, Y., Zhang, M., Wang, W. Thermal Properties of Acrylonitrile/Itaconic Acid Polymers in Oxidative and Nonoxidative Atmospheres. *Journal of Applied Polymer Science*, 116(2010)1207–1212

[7] Bhardwaj, N., Kundu, S. C. Electrospinning: A fascinating fiber fabrication technique. *Biotechnology Advances,* 28(2010)325–347

[8] Gu, S. Y., Ren, J., Vancso, G. J. Process optimization and empirical modeling for electrospun polyacrylonitrile (PAN) nanofiber precursor of carbon nanofibers. *European Polymer Journal,* 41 (2005) 2559–2568

[9] Wang, T., Kumar, S. Electrospinning of Polyacrylonitrile Nanofibers. *Journal of Applied Polymer Science*, 102(2006) 1023–1029

[10] Fang, J., Wang, H., Niu, H., Lin, T., Wang, X. Evolution of Fiber Morphologies during Poly (acrylonitrile) Electrospinning. *Macromol. Symp*., 287(2010)155–161

[11] Zhou, Z., Lai, C., Zhang, L., Qian, Y., Hou, H., Reneker, D. H., Fong, H. Development of carbon nanofibers from aligned electrospun polyacrylonitrile nanofiber bundles and characterization of their microstructural, electrical, and mechanical properties. *Polymer,* 50(2009) 2999–3006

[12] Zhou, Z., Liu, K., Lai, C., Zhang, L., Li, J., Hou, H., Reneker, D. H., Fong, H. Graphitic carbon nanofibers developed from bundles of aligned electrospun polyacrylonitrile nanofibers containing phosphoric acid. *Polymer*, 51 (2010)2360- 2367

[13] Hussain, D., Loyal, F., Greiner, A., Wendorff, J. H. Structure property correlations for electrospun nanofiber nonwovens. *Polymer,* 51(2010). 3989-3997

[14] Greiner, A. Wendorff, J.H. A fascinating method for the preparation of ultrathin fibers. *Angewandte Chemie International Edition*, 46(2007)5670-703.

[15] Gu, S.Y., Ren, J., Vancso, G. J. Process optimization and empirical modeling for electrospun polyacrylonitrile (PAN) nanofiber precursor of carbon nanofibers. *European Polymer Journal*, 41(2005)2559-2569.

[16] Moon, S C., Farris, R. J. Strong electrospun nanometer-diameter polyacrylonitrile carbon fiber yarns. *Carbon*, 47(2009)2829-39.

[17] Saum, M. Intermolecular association in organic nitriles; the CN dipole-pair bond. *Journal of Polymer Science*, 42, 139(1960) 57–66

[18] Ram, A. 1997, The Chemistry of Polymers, Fundamentals of Polymer Engineering, Plenum Press, New York

[19] Nuyken, O. ,2005, Polymers of acrylic acid, methacrylic acid, maleic acid and their derivatives Technische Universitat Munchen, Garching, Germany CSL Friebe - Handbook of polymer synthesis - CRC Press

[20] Sen, K., Hajir Bahrami, S., Bajaj, P. 1996, High-Performance Acrylic Fibers *JMS Rev Macromol Chem Phys,* C 36(1996)1-76

[21] Bhanu, V.A., Rangarajan, P., Wiles, K., Bortner, M., Sankarpandian, M., Godshall, D., Glass, T. E., Banthia, A. K., Yang, J., Wilkes, G., Baird, D., McGrath J. E. . Synthesis and characterization of acrylonitrile methyl acrylate statistical copolymers as melt processable carbon fiber precursors. *Polymer*, 43(2002) 4841–4850

[22] Mohammady, S. Z., Elkholy, S. S., and Elsabee, M. Z. Investigation of the relaxation behavior of novel terpolymers of acrylonitrile, methyl methacylate and indene, *Polym Int,* 56(2006) 7-13

[23] Bahrami, H., Bajaj, P., Sen. K. Acid Thermal Behavior of Acrylonitrile Carboxylic Acid Copolymers. *Journal of Applied Polymer Science,* Vol. 88(2003)685–698

[24] Yagci, Y., Menceloglu, Y., Baysal, B. M.,Gungor, A. Acrylonitrile block copolymers; Preparation of polyacrylonitrile containing azo-linkage in the main chain by anionic insertion polymerization. *A. Polymer Bulletin* 21(1989)259-263

[25] Qiu, G., Tang, Z., Huang, N. X., Chen, H. J. Investigations of the Copolymerization of Acrylonitrile with Vinyl Acetate and Sodium Methallylsulfonate. *Journal of Applied Polymer Science*, 82(2001) 854–860

[26] Yu, M., Chen, H., Liang, Y., Cui, H., Zhou, W., Cui, X., Li, D. Porous Acrylonitrile/Itaconic Acid Copolymers Prepared by Suspended Emulsion Polymerization. *Journal of Applied Polymer Science*, 111(2009) 2761–2768

[27] Devasia, R., Reghunadhan Nair C. P., Ninan, K. N. Solvent and kinetic penultimate unit effects in the copolymerization of acrylonitrile with itaconic acid. *European Polymer Journal,* 38(2002) 2003–2010

[28] Xu, Z. K., Kou, X., Liu, R. Q., Nie, Z. M., Xu, Y. Y. Incorporating alpha-allyl glucoside into polyacrylonitrile by water-phase precipitation copolymerization to reduce protein adsorption and cell adhesion. *Macromolecules,* 36(2003):2441-2447

[29] Nie, F. Q., Xu, Z. K., Wan, L. S., Ye, P., Wu, J. Acrylonitrile-based copolymers containing reactive groups: synthesis and preparation of ultrafiltration membranes. *Journal of Membrane Science*, 230(2003)1-11.

[30] Liu, T., De Simone, J. M., Roberts, G. W. Kinetics of the precipitation polymerization of acrylic acid in supercritical carbon dioxide: The locus of polymerization, *Chemical Engineering Science,* 61(2006) 3129 – 3139.

[31] Devasia, C. P., Nair, R., Sadhana, N. S., Babu, Ninan, K. N. Fourier Transform Infrared and Wide-Angle X-Ray Diffraction Studies of the Thermal Cyclization Reactions of High-Molar-Mass Poly(acrylonitrile-co-itaconic acid), *J. App Poly Sci,* 100(2006)3055–3062.

[32] Grassie, N., McGuchan, R. Pyrolysis of polyacrylonitrile and related polymers—VI. Acrylonitrile copolymers containing carboxylic acid and amide structures, *Eur Polym J,* 8(1972) 257-269.

[33] Ouyang, Q., Cheng, L., Wang, H., Li, K. Mechanism and kinetics of the stabilization reactions of itaconic acid-modified polyacrylonitrile Polymer Degradation and Stability, 93(2008)1415–1421

[34] Tsai, J. S., Lin, C. H. Polyacrylonitrile precursors by copolymer and additive with itaconic acid, Journal of Materıals Science Letters, 9(1990)869-871

[35] Zhao, Y., Wang, C., Yu, M., Cui, M., Wang, O., Zhu,B. Study on monomer reactivity ratios of acrylonitrile/itaconic acid in aqueous deposited copolymerization system initiated by ammonium persulfate. *J Polym Res*, 16(2009)437–442

[36] Devasia,R. Nair, R. Ninan, K.N. Copolymerization of acrylonitrile with itaconic acid in dimethylformamide: effect of triethylamine. *European Polymer Journal*, 39(2003) 537–544

[37] Wang, Z. G., Ke, B. B., Xu, Z. K. Covalent Immobilization of Redox Enzyme on Electrospun Nonwoven Poly(Acrylonitrile-co-Acrylic Acid) Nanofiber Mesh Filled With Carbon Nanotubes: A Comprehensive Study. *Biotechnology and Bioengineering*. 97(2007) 708-720.

[38] Huang, X. J., Yu, A. G., Jiang, J., Pan, C. Qian, J.W. Xu, Z.K. Surface Modification of Nanofibrous Poly(acrylonitrile-co-acrylic acid) Membrane with Biomacromolecules for Lipase Immobilization, *Journal of Molecular Catalysis B: Enzymatic.* 57(2009) 250-256.

[39] Ramakrishna, S., Fujihara, K., Teo, W. E., Lim, T. C., Ma, Z., 2005, An Introduction yo Electrospinning and Nanofibers, World Scientific Publishing Co. Pte. Ltd., Singapore.

[40] Bhardwaj, N., Kundu, S. C. Electrospinning: A fascinating fiber fabrication technique, *Biotechnology Advances.* 28(2010)325-347.

[41] Ramakrishna, S., Fujihara, K., Teo, W.E., Ma, Z.W. and Lim, T.C., ,2005. An Introduction to Electrospinning and Nanofibers, World Scientific Publishing Co. Pte. Ltd., ISBN 981-256-415-2.

[42] Göktaş, A., (2008). Electrospinning of Polystyrene/Butyl Rubber Blends: A Parametric Study' Postgraduate thesis.

[43] Cetiner, S., Kalaoglu, F., Karakas, H., Sarac, A.S. (2010). Electrospun Nanofibers of Polypyrrole-Poly(Acrylonitrile-co-Vinyl Acetate). *Textile Research Journal*, 80 (2010) 1784–1792

[44] Kalayci, V. E., Patra, P. K., Kim, Y. K., Ugbolue, S. C., Warner , S. B. Charge consequences in electrospun polyacrylonitrile (PAN) nanofibers, , *Polymer,* 46(2005) 7191–7200

[45] Buchko, C. J, Chen, L. C., Shen, Y., and Martin, D. C. Processing and microstructural characterization of porous biocompatible protein polymer thin films, *Polymer,* 40(1999) 7397-7407.

[46] Ultra-Web Media Technology, (n.d.) Date retrieved 25.06.2012, adress: http://www.donaldson.com/en/about/technology/index.html

[47] Nanoweb Advanced Nanofiber Technology, (n.d.) Date retrieved 25.06.2012, adress: http://www.hollingsworth-vose.com/products/nanoweb/index.html

[48] Reneker, D.H., Fong, H., Eds. 2003, Polymer nanofibers, Polymer Preprints, American Chemical Society.

[49] Senecal, K. J., Ziegler, D. P. Mosurkal,R. , Schreuder-Gibson, H. Samuelson, L.A. Photoelectric response from nanofibrous membranes. *Mater Res Soc Symp Proc*,708(2002).285–289.

[50] Norris, I. D. Shaker, M. M., Ko, F.K., Macdiarmid, A.G. Electrostatic fabrication of ultrafine conducting fibers: polyaniline/polyethylene oxide blends. *SyntheticMetals*, 114(2000). 109–114.

[51] Choi, S. W., Jo, S. M., Lee, W. S., Kim, Y. R. An electrospun poly (vinylidene fluoride) nanofibrous membrane and its battery applications. *Adv Mater;*15(2003)2027–2032.

[52] Kim, C. Electrochemical characterization of electrospun activated carbon nanofibres as an electrode in supercapacitors. *Journal of Power Sources,* 142(2005)382–388

[53] Kim, C., Yang, K. S. (2003) Electrochemical properties of carbon nanofiber web as an electrode for supercapacitor prepared by electrospinning, *Applied Physics Letters,* 83(2003)1216-1218

[54] Devasia, R., Reghunadhan Nair, C.P. and Ninan, K.N. (2003). Dilute solution viscosity properties of high molar mass poly(acrylonitrile-co-itaconic acid). *Polym Int*, 52(2003) 1519–1526

[55] Bercea, M. Morariua, Ioan, S. Ioan, C. Simionescu, B.C. Viscometric study of extremely dilute polyacrylonitrile Solutions, *European Polymer Journal,* 35(1999) 2019-2024

[56] Bajaj, P., Sreekumar, T.V. and Sen, K. . Effect of Reaction Medium on Radical Copolymerization of Acrylonitrile with Vinyl Acids, *Journal of Applied Polymer Science,* 79(2001) 1640–1652

[57] Devasia, R., Reghunadhan Nair, C. P., Ninan, K. N. Temperature and shear dependencies of rheology of poly(acrylonitrile-co-itaconic acid) dope in DMF, Polym. Adv. Technol.; 19(2008). 1771–1778

[58] Lee, J. M., Kang, S. J., Park, S. J. . Synthesis of Polyacrylonitrile Based Nanoparticles via Aqueous Dispersion Polymerization. Macromolecular Research, 17, 10(2009)817-820

[59] Bajaj, P., Sen, K., Hajir Bahrami, S. Solution Polymerization of Acrylonitrile with Vinyl Acids in Dimethylformamide, Journal of Applied Polymer Science, 59(1996) 1539-1550

[60] Ouyang, Q., Cheng, L., Wang, H. J., Li, K. X. Dsc Study Of Stabilization Reactions in Poly(Acrylonitrile– co–Itaconic Acid) with Peak-Resolving Method, Journal of Thermal Analysis and Calorimetry, 94 1(2008) 85–88

[61] Gupta, K., Paliwal, D. K., Bajaj, P. Effect of the Nature and Mole Fraction of Acidic Comonomer on the Stabilization of Polyacrylonitrile, *Journal of Applied Polymer Science*, 59(1996) 1819-1826

[62] Bajaj, P., Screekumar T. V., Sen, K.. Thermal behaviour of acrylonitrile copolymers having methacrylic and itaconic acid comonomers. *Polymer*, 42(2001) 1707-1718

[63] Gupta, A. K., Paliwal, D. K., Bajaj, P. Effect of an acidic comonomer on thermooxidative stabilization of polyacrylonitrile. *J Appl Polym Sci,* 58(1995) 1161-1174

[64] P. E. Milsom, J. L. Meers 1985, Gluconic and itaconic acids M. Moo-Young (Ed.), *Comprehensive Biotechnology*, vol. 3Pergamon Press, Oxford.

[65] Cetiner, S., Sen, S., Arman, B. and Sarac, A. S. Acrylonitrile/Vinyl Acetate Copolymer Nanofibers With Different Vinylacetate Content. J. Appl. Polym. Scı. 127(2012) 3830–3838,

Author' biography with Photo

Prof.Dr. A.Sezai SARAC – CURRICULUM VITAE

A.Sezai SARAC received his BSc, and MSc in Chem.Eng.from Istanbul Technical University, PhD. from University of Missouri-Rolla,USA in Chemistry (1976).He held postdoctoral position at University of Leeds –UK (1979-1980).He is a professor at Istanbul Technical University, Department of Chemistry, Polymer Science &Technology and Nanoscience & Nanoengineering graduate programs. .He was a visiting professor at Materials and Surface Science Institute University of Limerick in the period of 2002-2003,and was a Head of Physical Chemistry Division ,Head of Department of Chemistry between 1991 -1994, and Dean of Faculty of Science and Letters between 1994- 1997,Director of Polymer Science &Technology between 2004-2010.

He has authored about 200 scientific publications, and 8 review articles and book chapters, and ~170 conference contributions, with Citation number of 1720 and H index: 23.

He is awarded a Doctor (Honoris Causa) in Chemical Sciences , Tajikistan Academy of Sciences (2011) . He is in the Editorial Board of the Journal of Polymers (Since 2013) and The Scientific World Journal, Chemical Engineering,Hindawi Publishing Corporation (Since 2012) ,

Editorial Board of the "Materials Protection" /Zaštita Materijala Engineers Society of Corrosion (Since 2009)

His recent research interest on the thin conjugated polymeric nanofilms and nanofibers and their nanocomposites, Modified Carbon Fibers,Biosensor microelectrodes , electrocopolymerization and their surface characterizations. He has been awarded a number of grants and fellowsips: DAAD,DFG, NATO Collab. Res., TUBITAK Res., State Planning Organization Grants. Prof Sarac is recently a NATO Partner Director of SfP project 983931 (2011-2014) and TUBITAK-ASCR Int.Project -111T051(2012-2014)and working group member of CMST COST Action CM1101 WG4 (2012- 2016) and Management Committee Member of CMST COST Action CM1101 "Colloidal Aspects of Nanoscience for Innovative Processes and Materials ". *MPNS COST Action MP1206* "Electrospun Nano-fibres for bio inspired composite materials and innovative industrial applications" MC Substitute Member MO1206TR (2013-2016)